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⑯ **Organic solvent and water resistant, thermally, oxidatively and hydrolytically stable radiation-curable coatings for optical fibers, optical fibers coated therewith and processes for making same.**

⑯ Ultraviolet radiation-curable primary coating compositions for optical fibers are disclosed. The primary coatings comprise a polyether polyol-based reactively terminated aliphatic urethane oligomer; one or more diluent monomers terminated with at least one end group capable of reacting with the reactive terminus of the oligomer; an organofunctional silane adhesion promoter; and an optical photoinitiator. Also disclosed are optical fibers coated with the coatings of the invention, and processes for preparing same.

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after soaking in gasoline at room temperature for four hours, as a measure of organic solvent absorption.

It can be readily appreciated that the attainment of organic solvent resistance and water resistance are often at cross purposes, one more easily attained with a hydrophilic composition and the other with a hydrophobic composition, and thus difficulty achieved.

5 Furthermore, the coating should have optimized adhesion to its substrate, high enough that it will remain adhered thereto under use conditions, yet not so high as to impair strippability for splicing.

Similarly, the secondary coating must have a number of essential and optimal qualities. The secondary coating should function as a hard protective layer which allows the fiber not to be damaged during its processing and use, and thus should have a relatively high glass transition temperature (Tg) and a high 10 modulus. Furthermore, like the primary coating, the secondary coating should undergo minimal changes in physical properties on exposure to organic solvents and moisture. Moreover, secondary coatings should have a low coefficient of friction (COF) to facilitate winding and unwinding of the fibers on spools and to allow the fibers to slide easily along each other in a cable structure, thus relieving stress, but not so low as to result in a reduced tendency to stay aligned on the spool.

15 Again, in monocoat applications, the single coating layer should optimally have certain properties intermediate those typically seen in primary and secondary coatings, i.e., with respect to modulus, Tg and refractive index.

Still other properties exist which are desirable in both primary and secondary coatings. For example, fiber manufacturers are motivated to coat the fibers as rapidly as possible to attain the economy of faster 20 cure speeds, as these result in higher line speeds. The cure speeds of coating materials may be determined by constructing a UV dose versus modulus curve. The lowest UV dose at which the coating modulus exhibits dose independence is considered its cure speed. There is therefore a demand for faster curing coatings; for example, high line speeds are obtained with primary and secondary coatings which may be applied wet-on-wet and simultaneously ultraviolet light-cured. One way of doing this is described in U.S. 25 Patent 4,474,830, issued October 2, 1984 to Carl R. Taylor, which patent is expressly incorporated herein by reference.

Another desirable objective for both primary and secondary UV-curable coatings is to minimize the amount of unbound material in the coating after cure. Even when the cured coatings are considered 100% 30 solids, there may still exist a small amount of material which does not chemically bind into the polymer network on curing. Examples of such materials in the cured coatings include unreacted monomer, unreacted photoinitiator, certain non-functional additives and so forth. The presence of excessive amounts of such materials is undesirable, inasmuch as volatilization of such components over time may change the physical properties of the coating. For example, volatile materials from the primary coating may permeate into the secondary coating, tending to plasticize it and resulting in strength loss. Also, volatile materials may 35 cause production of unpleasant odors.

Still other important qualities of both optical fiber coatings are viscosity and shelf life. Good shelf life is considered formulation stability of at least six to twelve months. Viscosity can typically be somewhat 40 adjusted by regulation of the temperature at which the coatings are applied. However, it is advantageous to set the viscosity high enough so as to maintain proper rheology and handling of the coating on application, but low enough to facilitate bubble release and to minimize the amount of heat needed in the preparation. Excessive heating is undesirable inasmuch as it may result in premature gelling or viscosity buildup due to possible thermal initiation of polymerization.

PRIOR ART COATINGS

45 Various single or double layer fiber coatings exist in the prior art. Among these are epoxy- or urethane-based resins. However, many of these resins cure slowly; have poor moisture or organic solvent resistance or poor hydrolytic, thermal and oxidative stability; and have undesirable yellowing properties.

There have also been developed primary (buffer) coatings which cure on exposure to ultraviolet 50 radiation. Such prior art primary coatings, however, have conventionally not been very moisture resistant and have some of the same deficiencies as above. In general, coatings formulated for moisture resistance are not resistant to organic solvents, and vice versa.

To obviate these flaws, the primary-coated optical fibers of the prior art have been topcoated with a 55 tough and flexible overcoat which possesses superior resistance to moisture and abrasion. Prior art coatings have included extruded nylon "jacket" coatings, which are, however, more expensive and more difficult to apply than would be an ultraviolet-cured coating.

There have recently been developed optical fiber coats which are very moisture resistant and which have excellent thermal, hydrolytic and oxidative stability. Applicant's U.S. Serial No. 742,531, filed August 8,

The primary coating, when cured, should have, *inter alia*, the following properties: moisture resistance; organic solvent resistance; ease of application; acceptable adhesion without compromising strippability; low volatiles content; low tensile modulus over the life of the fiber; low glass transition temperature; and long shelf life. Furthermore, it should be transparent; nonmalodorous; fast curing; and remain adherent, even upon aging in high heat and humidity environments. Additionally, the cured primary coating should maintain its excellent properties under accelerated aging conditions of increased temperature and humidity as a measure of its long term thermal, hydrolytic and oxidative stability.

The present invention involves the recognition that it is possible, through the judicious choice of ingredients and proportions, to formulate a primary coating composition meeting these criteria.

The primary coating composition of the present invention contains four basic ingredients, (A), (B), (C) and (D).

(A.) The Polyether Polyol-Based Oligomer

The first ingredient is a reactively terminated polyether polyol-based urethane oligomer (A). This component comprises from about 10 percent to about 90 percent by weight of the composition base on the total weight of the (A), (B), (C) and (D) ingredients of the composition. Preferably, this oligomer comprises from about 20 percent to about 80 percent, and more preferably from about 30 percent to about 70 percent by weight of the composition, based on the total weight of the (A) through (D) ingredients.

The particular oligomer used in the present invention is chosen to impart good thermal, oxidative and hydrolytic stability to the system, as well as to confer both moisture and organic solvent resistance.

It has been known in the art that various types of UV-curable oligomers exist which may yield a soft, compliant, low glass transition temperature-type coating. Acrylate- or methacrylate-terminated monomers are particularly commonly used due to their ease of cure upon ultraviolet radiation. One system known in the art is acrylate-endcapped polybutadiene- type rubber or rubber-modified acrylated monomers as base resins. While these systems have excellent low temperature properties and are hydrophobic for moisture resistance, their internal carbon-carbon double bonds (unsaturation) make them susceptible to oxidation over a long period of time.

It is also known in the art to employ acrylated silicones as base resins in such compositions. While these have good low temperature properties and hydrophobicity, they are difficult to formulate with a suitably high refractive index; tend to have poor thermal stability; and may be susceptible to hydrogen outgassing which can lead to signal attenuation in fibers so coated.

Yet another system known in the art involves the use of acrylated fluorocarbons. While these are hydrophobic and thermally stable, they are typically incompatible with most non-halogenated organic compounds. Additionally, they are very expensive relative to other systems.

To overcome many of the disadvantages of the prior art systems, it may be tried to utilize a urethane system based on one of a variety of backbones. In general, urethane acrylate systems based on polyethers or polyesters were usually characterized by poor water resistance and by thermal instability. Additionally, known urethane oligomers based on aromatic isocyanates displayed thermal instability and tended to yellow. While polyether-based urethane acrylates have excellent low Tg properties, when used alone, many are not hydrophobic enough for optical fiber applications and are susceptible to oxidation. Polyester-based urethane acrylates, on the other hand, have good thermal stability but are susceptible to hydrolysis.

Thus, the present invention uses an oligomer which, in combination with the other components of this invention, obviates many of the above problems.

The oligomer (A) utilized in the present invention is the reaction product of (i) a polyether polyol; (ii) an aliphatic polyisocyanate; and (iii) an endcapping monomer capable of supplying a reactive terminus.

The oligomeric component may contain very small amounts of urethane acrylates based on polyesters, but preferably contains only polyether-based oligomers, for optimal long term stability.

The polyether polyol is based on a straight chained or branched alkylene oxide of from one to about twelve carbon atoms. The polyether polyol may be prepared by any method known in the art.

The polyisocyanate component (ii) is non-aromatic. Oligomers based on aromatic polyisocyanates effect yellowing in the cured coating. Non-aromatic polyisocyanates of from 4 to 20 carbon atoms may be employed. Suitable saturated aliphatic polyisocyanates include but are not limited to isophorone diisocyanate; dicyclohexylmethane-4,4'-diisocyanate; 1,4-tetramethylene diisocyanate; 1,5-pentamethylene diisocyanate; 1,6-hexamethylene diisocyanate; 1,7-heptamethylene diisocyanate; 1,8-octamethylene diisocyanate; 1,9-nanamethylene diisocyanate; 1,10-decamethylene diisocyanate; 2,2,4-trimethyl- 1,5-pentamethylene diisocyanate; 2,2'-dimethyl-1,5- pentamethylene diisocyanate; 3-methoxy-1,6-hexamethylene diisocyanate; omega, omega'-dipropylether diisocyanate; 1,4-

of -27°C.

Methacrylate equivalents of these oligomers may also be used.

(D) Uvithane® ZL-1178 oligomer from Morton Thiokol, Inc., Morton Chemical Division, Princeton, New Jersey, polyether based aliphatic urethane acrylate. This oligomer has a viscosity of 55-75 poises at 5 120°F and 700-800 poises at 78°F and, when cured neat, has a tensile strength of 325 psi and an ultimate elongation of 45%. The methacrylate analog of this monomer may be used as well.

(5) Furthermore, any polyether-based aliphatic urethane acrylate or methacrylate oligomer of the type exemplified above is believed to be suitable so long as the desirable properties of the claimed 10 composition are not adversely effected.

10 The primary coating containing the oligomer of this invention has a water absorption value of less than about 5% by weight, and preferably less than about 3%. Furthermore, the coating should swell less than 40% in length, and preferably less than about 35% in length, when soaked in gasoline for about 4 hours at room temperature.

15 (B.) The Diluent Monomer

The second essential component of the composition is a diluent monomer which is terminated with at least one end group capable of reacting with the reactive terminus of (A). Again, this terminus is preferably acrylate or methacrylate.

20 The monomer is selected to be one that will adjust the total primary coating composition to a viscosity in the range of about 1,000 cps (centipoises) to about 10,000 cps, and preferably in the range of about 4,000 cps to about 8,000 cps, measured by a Brookfield viscometer, model LVT, spindle speed of 6 rpm, spindle #34, at 25°C. Additionally, it is chosen to be soft-curing and to have a low Tg, thus lowering the Tg 25 of the composition. Furthermore, a specific diluent may be chosen which is capable of adjusting the refractive index of the whole composition, as will be further discussed below.

The monomer (B) comprises from about 5 percent to about 80 percent by weight of the composition, based on the total weight of (A), (B), (C) and (D). Preferably, it comprises from about 10 percent to about 70 percent, and more preferably from about 10 percent to about 60 percent by weight of the composition, based upon the total weight of (A), (B), (C) and (D).

30 This diluent monomer may be either straight chained or branched, and should preferably be at least partially aliphatic. One type of diluent which may be used is an alkyl acrylate or methacrylate having about 6 to 18 carbon atoms in the alkyl moiety of the molecule.

35 Suitable examples of such monomers include but are not limited to acrylates and methacrylates such as hexyl acrylate; hexyl methacrylate; 2-ethylhexyl acrylate; 2-ethylhexyl methacrylate; isooctyl acrylate; isooctyl methacrylate; octyl acrylate; octyl methacrylate; decyl acrylate; decyl methacrylate; isodecyl acrylate; isodecyl methacrylate; lauryl acrylate; lauryl methacrylate; tridecyl acrylate; tridecyl methacrylate; palmitic acrylate; palmitic methacrylate; stearyl acrylate; stearyl methacrylate; C₁₄-C₁₅ hydrocarbon diol diacrylates; C₁₄-C₁₅ hydrocarbon diol dimethacrylates; and mixtures of the above.

40 Preferred alkyl acrylate monomers include stearyl acrylate, lauryl acrylate and isodecyl acrylate. A particularly preferred one is lauryl acrylate.

As mentioned above, the diluent monomer may also be one which is capable of adjusting the refractive index of the composition. Such monomers, when used, may, for example, contain (1) an aromatic moiety; (2) a moiety providing a reactive (e.g., acrylic or methacrylic) group; and (3) a hydrocarbon moiety.

45 The aromatic moiety of such refractive index modifying monomer (B) is itself capable of raising the refractive index; however, the hydrocarbon moiety may assist in increasing the compatibility of this monomer with the oligomer (A). The moiety providing a reactive group (e.g., an acrylate or methacrylate group) renders the compound compatible with the system as a whole, inasmuch as it has available reactive termination which allows it to crosslink with the rest of the composition upon ultraviolet curing, thus minimizing the volatiles content of the cured system. Samples of aromatic monomers additionally containing 50 hydrocarbon character and a vinyl group include but are not limited to polyalkylene glycol nonylphenylether acrylates such as polyethylene glycol nonylphenylether acrylate or polypropylene glycol nonylphenylether acrylate; polyalkylene glycol nonylphenylether methacrylates such as polyethylene glycol nonylphenylether methacrylate or polypropylene glycol nonylphenylether methacrylate; and mixtures of these.

55 In each case, the phenyl group serves to increase the refractive index of the coating and the nonyl component renders the composition somewhat more compatible with the aliphatic oligomer (A). This monomer is capable of increasing the refractive index of the composition relative to that of a composition comprising only (A), (C) and (D). A suitable primary coating composition may, for example, have a refractive index of greater than or equal to about 1.48.

Suitable photoinitiators include but are not limited to the following: hydroxycyclohexylphenyl ketone; hydroxymethylphenyl propanone; dimethoxyphenylacetophenone; 2-methyl-1-[4-(methyl thio)phenyl]-2-morpholino-propanone-1; 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one; 1-(4-dodecylphenyl)-2-hydroxy-2-methylpropan-1-one; 4-(2-hydroxyethoxy)phenyl-2(2-hydroxy-2-propyl)ketone; diethoxyphenyl acetophenone; and mixtures of these.

The photoinitiator preferably comprises from about 1.0 percent to about 10.0 percent by weight of the composition, based upon the total composition of the (A) through (D) ingredients. Preferably, the amount of photoinitiator is from about 1.5 percent to about 8.0 percent, and more preferably from about 2.0 percent to about 7.0 percent by weight, based upon total weight of (A), (B), (C) and (D) ingredients.

A particularly preferred photoinitiator is hydroxycyclohexylphenyl ketone. The photoinitiator should be chosen such that a cure speed, as measured in a dose versus modulus curve, of less than 1.0 J/cm², and preferably less than 0.5 J/cm², is required, when the photoinitiator is used in the designated amount.

Other Optional Components

Various optional components may be used in the primary coating beyond the (A) through (D) components which are described above. For example, optional chain transfer agents (E) may be used to control the modulus and glass transition temperature of the coating. One way known in the art to control the molecular weight and, consequently, the modulus and glass transition temperature of a polymerization product is to use one or more chain transfer agents. The addition of a chain transfer agent to a formulation lowers the molecular weight of a polymer produced and results in a lower modulus, lower glass transition temperature coating.

Preferred chain transfer agents are mercapto compounds, optionally having a hydrocarbon chain of at least eight carbon atoms. Examples of suitable mercapto chain transfer agents include but are not limited to methyl thioglycolate; methyl-3-mercaptopropionate; ethyl thioglycolate; butyl thioglycolate; butyl-3-mercaptopropionate; isoctyl thioglycolate; isoctyl-3-mercaptopropionate; isodecyl thioglycolate; isodecyl-3-mercaptopropionate; dodecyl thioglycolate; dodecyl-3-mercaptopropionate; octadecyl thioglycolate; and octadecyl-3-mercaptopropionate. Parathiocresol; thioglycolic acid; and 3-mercaptopropionic acid may also be used, but may display some incompatibility with the resin and may produce odor problems. In general, lower molecular weight chain transfer agents are preferred.

A particularly preferred chain transfer agent is isoctyl-3-mercaptopropionate (IOMP).

The chain transfer agent may, if used, comprise from about 0.1 percent to about 10.0 percent by weight of the composition based upon the total weight of ingredients (A) through (D). Preferably, the chain transfer agent comprises from about 0.25 percent to about 9.0 percent by weight, and still more preferably from about 0.5 percent to about 8.0 percent by weight, based on the total weight of the (A), (B), (C) and (D) components.

To improve shelf life (storage stability) of the uncured coating, as well as to increase thermal and oxidative stability of the cured coating, one or more stabilizers (F) may be included in the composition. Examples of suitable stabilizers include tertiary amines such as diethylethanolamine, diethyl hydroxyl amine and trihexylamine; hindered amines; organic phosphites; hindered phenols; mixtures thereof; and the like. Some particular examples of antioxidants which can be used, alone or in combination, include but are not limited to octadecyl-3(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate; thiodiethylene bis (3,5-di-tert-butyl-4-hydroxy) hydrocinnamate; butylated paracresol-dicyclopentadiene copolymer and tetrakis [methylene (3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane. Additionally, certain silanes in small quantities, e.g., as low as 0.0001 percent to 0.01 percent by weight, may be used as stabilizers. An example of a suitable silane is 3-aminopropyl trimethoxysilane.

When a stabilizer is used, it may be incorporated in a total amount of from about 0.0001 percent to about 3.0 percent, based on the weight of the (A) through (D) ingredients. Preferably, it is included in the range from about 0.25 percent to about 2.0 percent by weight, and more preferably in the range from about 0.5 percent to about 1.5 percent by weight, based on the total weight of the (A) through (D) ingredients. Desirable properties of a stabilizer include (1) non-migration (probably enhanced by low polarity and high molecular weight) and (2) basicity (to allow it to help in neutralizing residual acid which might prematurely initiate polymerization). Preferred stabilizers include thiodiethylene bis (3,5-di-tert-butyl-4-hydroxy) hydrocinnamate and 3-aminopropyl trimethoxysilane.

than about 40 percent when soaked in gasoline at room temperature for four hours and a water absorption value of no more than about 5 % by weight; and

(2) radiation-curing said coating *in situ*.

The reactive termini of (A) and (B) are preferably selected from acrylate and methacrylate.

5 In one embodiment, the process comprises applying only the primary coating of the invention to the optical fiber and radiation-curing the coating *in situ*.

In an alternative embodiment, a secondary coating may be applied atop the primary coating of this invention, and the two coatings simultaneously radiation cured.

10 The primary and/or secondary coatings may be applied and cured by any method known in the art. A preferred method, whereby two coatings are applied wet-on-wet, is disclosed in U.S. Patent 4,474,830 to C. Taylor of AT&T Bell Laboratories. The coating or coatings may then be cured *in situ*, preferably by ultraviolet irradiation, to obtain a cured polymeric coating. Alternatively, the primary coating may be applied and cured, after which the secondary coating may be applied and cured.

15 COATED OPTICAL FIBERS OF THE INVENTION

The invention further relates to optical fibers, and especially to glass optical fibers, that are coated with the primary coating of this invention alone, or coated with the primary coating of this invention and a secondary coating.

20 In one embodiment, the invention is a coated optical fiber comprising:

(a) a glass optical fiber;

(b) a radiation cured primary coating layer comprising the cured reaction product of:

(A) from about 10 percent to about 90 percent by weight of a reactively terminated urethane oligomer which is the reaction product of (i) a polymer polyol, (ii) an aliphatic polyisocyanate, and (iii) an 25 endcapping monomer capable of supplying a reactive terminus;

(B) from about 5 percent to about 80 percent by weight of one or more monomer diluents which are terminated with at least one end group capable of reacting with the reactive terminus of (A);

(C) from about 0.1 to about 3.0 percent by weight of an organofunctional silane adhesion promoter; and

30 (D) optionally, from about 1.0 percent to about 10.0 percent by weight of a photoinitiator,

wherein all of the stated percentages are percentages by weight based on total weight of (A), (B), (C) and (D); and

(c) a radiation cured secondary coating layer comprising the cured reaction product of

(I) from about 10 percent to about 90 percent by weight of an aliphatic urethane oligomer based on a 35 polyester and/or polyether and containing a reactive terminus;

(II) from about 20 percent to about 60 percent by weight of hydrocarbonaceous viscosity-adjusting component capable of reacting with the reactive terminus of (I);

(III) optionally, from about 0.05 percent to about 10.0 percent by weight of a photoinitiator, wherein all 40 of the stated percentages are percentages by weight based on total weight of (I), (II) and (III).

In a preferred embodiment, the invention is a coated optical fiber comprising:

(a) a glass optical fiber;

(b) a radiation-cured primary coating layer comprising the cured reaction product of

(A) from about 10 percent to about 90 percent by weight of an acrylated or methacrylated urethane oligomer which is the reaction product of (i) a polyether polyol; (ii) an aliphatic polyisocyanate; and (iii) an 45 endcapping monomer selected from the group consisting of hydroxyalkylacrylate and hydroxyalkylmethacrylate;

(B) from about 5 percent to about 80 percent by weight of one or more acrylate or methacrylate monomer diluents;

(C) from about 0.1 percent to about 3.0 percent by weight of an organofunctional silane adhesion promoter; and

(D) optionally, from about 1.0 percent to about 10 percent by weight of a photoinitiator,

wherein all of the stated percentages are percentages by weight based on total weight of (A), (B), (C) and (D); and

(c) a radiation-cured secondary coating layer comprising the cured reaction product of

(I) from about 40 percent to about 80 percent by weight of a mixture of aliphatic urethane acrylate oligomers based on polyether backbones;

(II) from about 25 percent to about 50 percent by weight of a mixture of isobornyl acrylate and hexanediol diacrylate; and

Unless otherwise noted, throughout the Examples and the remainder of this application, "modulus" refers to 2.5% tensile modulus, measured using an Instron tensile tester. Unlike in the remainder of the application, where percentage by weight referred to the total weight of the (A) through (D) ingredients, parts by weight in the Examples refers to the total composition described in that Example, including all components. The optional ingredients are identified by an asterisk (*) in the Examples. It should be noted that, although the specification teaches that the photoinitiator is optional, it is required in the Examples, all of which employ ultraviolet cure. The other components are essential for use, if the exemplified coating is to meet the rigorous requirements for a commercially acceptable coating for optical glass fiber.

10 Example I

A Primary Coating Having Good Organic Solvent and Water Resistance Which is Thermally, Hydrolytically and Oxidatively Stable

15 The following composition was formulated:

Ingredient	Parts by Weight
20 ALU-351 polyether-based aliphatic urethane acrylate oligomer based on polytetramethylene polyol (from Echo Resins and Laboratory, Versailles, MO)(A)	60.0
25 Aronix M-111 polyethylene glycol nonylphenylether acrylate monomer (from Toagasei Chemical Industry Company Ltd., Tokyo, Japan)(B)	approx. 21.00
30 lauryl acrylate monomer (B)	4.20
35 A-172 vinyl-tris-(2-methoxyethoxy silane) adhesion promoter (from Union Carbide Corp., Danbury, CT.) (C)	0.80
Irgacure 184 hydroxycyclohexyl phenyl ketone photoinitiator (from Ciba Geigy Corp., Hawthorne, NY.) (D)	6.00
Isooctyl 3-mercaptopropionate chain transfer agent (E)*	7.00
Irganox 1035 thiodiethylene bis-(3,5-di-tert-butyl-4-hydroxy) hydrocinnamate antioxidant and thermal stabilizer (from Ciba Geigy) (F)*	1.00
A-1110 3-aminopropyl trimethoxysilane shelf stabilizer (from Union Carbide) (F)*	0.00375

35 The uncured coating composition had the following viscosity values at these temperatures, measured by a Brookfield viscometer, model LVT, 6 rpm, # 34 spindle: 4250 cps at 25 °C; 3360 cps at 28 °C; 2810 cps at 30 °C; 1940 cps at 35 °C; and 1305 cps at 40 °C. The uncured composition had a refractive index of 1.4870 at 24.2 °C and a density of 8.66 lb/gal (1.04 g/cc).

40 A 6 mil coating of this composition was applied to a flat glass sheet using a Bird applicator and cured in air at 0.7 J/cm² using a 200-watts-per-inch-medium-pressure mercury vapor lamp.

Oxidative induction temperature was measured as follows. A sample of the above coating was subjected to differential scanning calorimetry under oxygen at a flow rate of 20 cc/min. Approximately 10 milligram samples were heated in open pans by increasing the temperature at a rate of 10 °C/minute from 100 °C to exotherm. The oxidative inductive temperature, or the point at which the exotherm began, was 200 °C.

45 The cured film had a rupture strength of 91.1 psi; elongation at break of 67.5%; TGA volatiles content of 6.53%; and a cured film refractive index of 1.4974 at 24.2 °C. Its glass transition temperature, as measured by differential scanning calorimetry, was broad and indistinct. Its cure ratio (ratio of 2.5% moduli at 25 °C when cured in air at 0.2 J/cm² and at 0.7 J/cm², respectively) was 79.7%.

The effect of temperature on 2.5% modulus of the cured film was as follows: 25 °C: 190.1 psi; 0 °C: 178.0 psi; -20 °C: 403.7 psi; -40 °C: 21,643.0 psi; and -60 °C: 188,003.0 psi.

50 Water absorption of the sample was measured as follows. The cured film was equilibrated at 50% (±5%) relative humidity and 23 °C (±2 °C) for 48 hours. After this conditioning, the sample was weighed and a weight "A" recorded. The sample was then soaked for 24 hours at 25 °C in distilled water, then patted dry and weighed; this weight was recorded as "B". The sample was next placed in a vacuum desiccator under 10 mmHg pressure at 25 °C for 24 hours, removed and again equilibrated at 50% (±5%) relative humidity and 23 °C (±2 °C) for 48 hours and weighed; this third weight was recorded as "C". Percent water absorption measured as B-C/A × 100 was about 1.78% for an average of three samples. This value is referred to as the water absorption value.

55 Other samples of this 6 mil thick coating were tested as follows to determine the effect of accelerated aging on various properties. Samples were conditioned for 48 hours at 50% (±5%) relative humidity and

This coating composition, before cure, had the following temperature/viscosity profile, measured by a Brookfield viscometer, model LVT, 6 rpm, # 34 spindle: 4720 cps at 25°C; 3780 cps at 28°C; 3070 cps at 30°C; 2060 cps at 35°C; and 1385 cps at 40°C. The liquid composition had a refractive index of 1.4908 at 25°C and a density of 8.58 lb/gal (1.03 g/cc).

5 A 6 mil coating of this composition was cast and cured as in Example I.

The cured film of this Example had a rupture strength of 82.6 psi; elongation at break of 57.4%; TGA volatiles content of 6.37%; oxidative induction temperature of 205°C; and a cured film refractive index of 1.5014 at 25°C. Its glass transition temperature was -31.7°C (midpoint) (-35.8°C onset) and its cure ratio (as described in Example I) was 85.9%.

10 The effect of temperature on 2.5% modulus was as follows for the cured film: 25°C: 226.0 psi; 0°C: 217.0 psi; -20°C: 777.4 psi; -40°C: 71,796.0 psi; and -60°C: 222,675.0 psi.

An excellent value for water absorption of 1.40% was measured in the manner described in Example I, after a 24 hour soak, as an average of three samples.

Other samples of this coating were tested under the same accelerated aging conditions as in Example I.

15 The following properties were observed for the cured coating described in this Example:

	125°C 7 days	93.3°C 10 days	93.3°C 10 days 95% RH	93.3°C 30 days	30 days 95% RH
20 weight change (%)	-6.89	-6.42	-0.89	-6.50	0.23
Tg (midpoint)(°C)	-29.4	-29.6	-32.8	-28.4	-33.9
2.5% modulus at 25°C (psi)	229.5	229.3	220.0	236.1	173.0
2.5% modulus change, % at 25°C	6.8	6.7	2.4	9.9	-19.5
25 rupture strength (psi)	126.1	137.6	93.4	117.2	90.7
% elongation at break	88.6	81.2	64.0	73.3	63.7

Glass adhesion, a measure of strippability, was measured at about 84 grams of force at 50% relative humidity and about 28 grams at 95% relative humidity, considerably higher than the comparable values in Example I.

30 However, a percent change of only 31.2% was measured in the gasoline swell test, slightly superior to Example I.

EXAMPLE III

35 A Primary Coating Having Organic Solvent and Water Resistance Which is Thermally, Hydrolytically and Oxidatively Stable

The following composition was made up:

40 Ingredient	Parts by Weight
ALU-351 polyether-based aliphatic acrylate oligomer based on polytetramethylene polyol (from Echo Resins and Laboratory)(A)	56.00
45 Aronix M-117 polypropylene glycol nonylphenylether acrylate monomer (from Toagasei) (B)	about 32.50
A-172 vinyl-tris-(2-methoxyethoxy silane) adhesion promoter (from Union Carbide) (C)	1.00
50 Irgacure 184 hydroxycyclohexyl phenyl ketone photoinitiator (from Ciba-Geigy) (D)	4.00
Isooctyl-3-mercaptopropionate chain transfer agent (E)*	5.50
55 Irganox 1035 thiodiethylene bis-(3,5-di-tert-butyl-4-hydroxy) hydrocinnamate antioxidant and thermal stabilizer (from Ciba-Geigy) (F)*	1.00
A-1110 3-aminopropyl trimethoxysilane shelf stabilizer (from Union Carbide) (F)*	0.00375

Before cure, the coating composition of this Example had the following temperature/viscosity profile, measured by Brookfield viscometer, model LVT, 6 rpm, # 34 spindle: 25°C:5440 cps; 28°C:4280 cps;

EXAMPLE VA Composition Having Good Aging Characteristics But Less Than Optimal Swelling

5 The following composition, similar to that of Example II, was made up:

Ingredient	Parts by Weight
ALU-353 polyether-based aliphatic urethane acrylate oligomer analogous to the oligomer of Example II except having a molecular weight about 2.0 times that of ALU-351, a higher viscosity and a lower modulus (from Echo Resins) (A)	36.75
Aronix M-111 polyethylene glycol nonylphenylether acrylate monomer (from Toagasei) (B)	55.00
A-172 vinyl-tris-(2-methoxyethoxy silane) (from Union Carbide) (C)	1.00
Irgacure 184 hydroxycyclohexyl phenyl ketone photoinitiator (from Ciba Geigy) (D)	6.00
Iooctyl-3-mercaptopropionate chain transfer agent (E) *	0.25
Irganox 1035 thiodiethylene bis-(3,5-di-tert-butyl-4-hydroxy) hydrocinnamate stabilizer (from Ciba Geigy) (F) *	1.00

20 The uncured coating had a viscosity of 5050 cps at 25 °C and a cure ratio of 82.4%. The composition, when cast, cured and subjected to the accelerated aging conditions of Example 1, performed well, but had a swelling value of 46.0%. This is believed to be a somewhat deleterious result of using a higher molecular weight oligomer.

EXAMPLE VIA Composition Exhibiting Low Swelling Prepared from A Mixture of Oligomers and Absent a Chain Transfer Agent

30 The following composition was made:

Ingredient	Parts by Weight
ALU-354 polyether-based aliphatic urethane acrylate oligomer analogous to that of Example I, but having a molecular weight about 2.6 times as high (from Echo Resins) (A)	20.00
Uvithane ZL-1178 polyether-based aliphatic urethane acrylate oligomer (from Morton Thiokol Inc., Princeton, NJ) (A)	20.00
Aronix M-111 polyethylene glycol nonylphenylether acrylate (from Toagasei) (B)	52.00
A172 vinyl-tris-(2-methoxyethoxy silane) (from Union Carbide) (C)	1.00
Irgacure 184 hydroxy cyclohexylphenyl ketone photoinitiator from (Ciba Geigy) (D)	6.00
Irganox 1035 thiodiethylene bis-(3,5-di-tert-butyl-4- hydroxy) hydrocinnamate stabilizer (from Ciba Geigy) (F)*	1.00

45 The composition had a viscosity of 6420 cps at 25 °C and a modulus of 264.3 psi. When cast, cured and tested as in previous Examples, a gasoline swelling measurement of 36.7% was recorded.

50

55

EXAMPLE IXAnother Composition Which Performed Well On Long Term Thermal Aging

5 The following composition was made up:

	Ingredient	Parts by Weight
10	Purelast® 566 polyether-based aliphatic urethane acrylate oligomer (from Polymer Systems Corp.) (A)	64.00
	Aronix M-117 polypropylene glycol nonylphenylether acrylate (from Toagasei) (B)	20.00
15	lauryl acrylate (B)	10.00
	A-172 vinyl-tris (2-methoxyethoxy silane) adhesion promoter (from Union Carbide) (C)	1.00
	Darocur 1173 hydroxymethylphenyl propanone photoinitiator (from Ciba Geigy) (D)	4.00
20	Irganox 1010 tetrakis [methylene (3,5-di-tert-butyl-4-hydroxy-hydrocinnamase)]methane	1.00

This composition had a viscosity of 4920 cps at 25 °C. It was cast and cured as in previous Examples, and, after cure, had a cure ratio of 55.3%. It performed well after dry aging at 125 °C for 7 days.

EXAMPLE XA Composition Having Good Solvent Resistance and Higher Adhesion

25 The following composition was made up:

	Ingredient	Parts by Weight
30	Purelast® 590 polyether-based aliphatic urethane acrylate oligomer (from Polymer Systems Corp.) (A)	46.00
35	Aronix M-111 polyethylene glycol nonylphenylether acrylate monomer (from Toagasei) (B)	39.95
	Lauryl acrylate (B)	5.00
	A-172 vinyl-tris-(2-methoxyethoxy silane) adhesion promoter (from Union Carbide) (C)	1.00
40	Irgacure 184 hydroxycyclohexylphenyl ketone photoinitiator (from Ciba Geigy) (D)	4.00
	Iooctyl-3-mercaptopropionate chain transfer agent (E)*	3.00
	Irganox 1035 thiobis (3,5-di-tert-butyl-4-hydroxy) hydrocinnamate stabilizer (from Ciba Geigy) (F)*	1.00
45	A-1110 3-aminopropyl trimethoxysilane stabilizer (F)	0.05

The uncured composition had a viscosity of 4900 cps at 25 °C.

When cast and cured as in previous Examples, the composition exhibited a 2.5% modulus at 25 °C of 149.2 psi; swelled only 26.5% in length after soaking in gasoline at room temperature for 4 hours; and 50 required 198.9 grams of force to peel at 50% relative humidity. It is expected to perform well on long term aging.

Example XIIAnother Secondary Coating Formulation

5 The following coating composition was prepared:

Ingredient	Parts by Weight
Photomer 6008 aliphatic urethane acrylate oligomer with polyether backbone, having an acrylate functionality of 2.6 (from Henkel Corporation)	34.00
AB2010A aliphatic urethane acrylate oligomer with polyether backbone, having an acrylate functionality of 2.4 (from American Biltrite Inc.)	34.00
Hexanediol diacrylate	13.99
Isobornyl acrylate	13.00
Irgacure 184 hydroxycyclohexylphenyl ketone photoinitiator (from Ciba Geigy)	4.00
Irganox 1035 thiodiethylene bis (3,5-di-tert-butyl-4- hydroxy) hydrocinnamate stabilizer (from Ciba Geigy)	1.00
DC57 surface tension adjustment additive (from Dow Corning)	0.01

20 The uncured coating of this Example had a refractive index of 1.4856 at 24.2 °C and a viscosity of 5320 cps at 25 °C.

25 A 6 mil coating was cast and cured as in previous Examples to produce a cured film having an oxidative induction temperature of 194 °C and a cure ratio (ratio of 2.5% moduli at 25 °C when cured in air at 0.2 J/cm² and at 0.7 J/cm², respectively) of 100.9%.

20 The coating, which is very similar to that of the previous Example, is expected to perform equally well on long term aging, and is similarly well suited for use as a secondary coating atop the primary coatings of the invention.

30 COMPARATIVE EXAMPLE IA Primary Coating Composition Which Aged Poorly

35 The following composition was formulated:

Ingredient	Parts by Weight
CN-966 polyester-based aliphatic urethane acrylate oligomer (from Sartomer Company) (A)	45.00
Aronix M-111 polyethylene glycol nonylphenylether acrylate (from Toagasei Chemical Industry Company, Ltd.) (B)	34.50
lauryl acrylate (B)	11.00
Chemlink-2000 50-50 mixture of linear C14 and C15 diol diacrylates (from Sartomer Company, Exton, PA) (B)	1.50
A-172 vinyl-tris(2-methoxyethoxy silane) (from Union Carbide) (C)	1.00
Irgacure 184 hydroxycyclohexylphenyl ketone photoinitiator (D)	6.00
Irganox 1076 octadecyl-3,5-(di-tert-butyl-4-hydroxy)hydrocinnamate stabilizer (from Ciba Geigy) (F)*	1.00

50 The liquid coating had an acceptable viscosity of 4630 cps at 25 °C, and a good cure ratio of 62.4%, but, when cast on a glass sheet as a 6 mil coating, cured, and subjected to the accelerated aging tests described in Example I, performed very poorly under high humidity and/or high temperature conditions.

refractive index of the composition relative to that of a composition containing only (A), (C) and (D); and
 (iii) mixtures thereof.

5 6. A radiation-curable coating composition according to any one of claims 1 to 5, wherein said monomer
 (B) is selected from the group consisting of hexyl acrylate; hexyl methacrylate; 2-ethylhexyl acrylate; 2-
 10 ethylhexyl methacrylate; isoctyl acrylate; isoctyl methacrylate; octyl acrylate; octyl methacrylate;
 decyl acrylate; decyl methacrylate; isodecyl acrylate; isodecyl methacrylate; lauryl acrylate; lauryl
 15 methacrylate; tridecyl acrylate; tridecyl methacrylate; palmitic acrylate; palmitic methacrylate; stearyl
 acrylate; stearyl methacrylate; C₁₄-C₁₅ hydrocarbon diol diacrylates; C₁₄-C₁₅ hydrocarbon diol
 20 dimethacrylates; polyalkylene glycol nonylphenylether acrylates; polyalkylene glycol nonylphenylether
 methacrylates; and mixtures thereof.

7. A radiation-curable coating composition according to any one of claims 1 to 5, wherein said monomer
 25 component (B) comprises a mixture of
 (i) a monomer selected from the group consisting of lauryl acrylate; stearyl acrylate; isodecyl
 acrylate; and mixtures thereof, and
 (ii) a monomer selected from the group consisting of polyethylene glycol nonylphenylether acrylate;
 30 polypropylene glycol nonylphenylether acrylate; and mixtures thereof.

8. A radiation-curable coating composition according to any one of claims 1 to 7, wherein said silane
 adhesion promoter (C) is selected from the group consisting of amino-functional silanes; mercapto-
 35 functional silanes; methacrylate-functional silanes; acrylamido-functional silanes; allyl-functional silanes;
 vinyl-functional silanes; acrylate-functional silanes; and mixtures thereof.

9. A radiation-curable coating composition according to claim 8, wherein said silane adhesion promoter
 (C) is selected from the group consisting of mercaptoalkyl trialkoxy silane; vinyl alkoxy silane;
 40 methacryloxyalkylalkoxy silane; aminoalkyl trialkoxy silane; and mixtures thereof.

10. A radiation-curable coating composition according to claim 9, wherein said silane adhesion promoter
 (C) is vinyl-tris-(2-methoxyethoxy silane).

11. A radiation-curable coating composition according to any one of claims 1 to 10, wherein said
 45 photoinitiator (D) is selected from the group consisting of hydroxycyclohexylphenyl ketone; hydroxymethylphenyl propanone; dimethoxyphenyl acetophenone; 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one; 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one; 1-(4-dodecylphenyl)-2-hydroxy-2-methylpropan-1-one; 4-(2-hydroxyethoxy) phenyl-2-(2-hydroxy-2-propyl)ketone; diethoxyacetophenone; 2,2-di-sec-butoxyacetophenone; diethoxyphenyl acetophenone; and mixtures thereof.

12. A radiation-curable coating composition according to claim 11, wherein said photoinitiator (D) is
 50 hydroxycyclohexylphenyl ketone.

13. A radiation-curable coating composition according to any one of claims 1 to 12, additionally comprising
 55 from 0.1% to 10% by weight, based on total weight of (A), (B), (C) and (D), of a mercapto functional
 chain transfer agent (E).

14. A radiation-curable coating composition according to claim 13, wherein said chain transfer agent (F) is
 60 selected from the group consisting of methyl thioglycolate; methyl-3-mercaptopropionate; ethyl
 thioglycolate; butyl thioglycolate; butyl-3-mercaptopropionate; isoctyl thioglycolate; isoctyl
 thioglycolate; isoctyl-3-mercaptopropionate; isodecyl thioglycolate; isodecyl-3-mercaptopropionate;
 65 dodecyl thioglycolate; dodecyl-3-mercaptopropionate; octadecyl thioglycolate; octadecyl-3-mercaptopropionate;
 and mixtures thereof.

15. A radiation-curable coating composition according to claim 14, wherein said chain transfer agent is
 70 isoctyl-3-mercaptopropionate.

16. A radiation-curable coating composition according to any one of claims 1 to 15, additionally comprising
 75 from 0.0001% to 3.0% by weight, based on total weight of (A), (B), (C) and (D), of a stabiliser (F)

26. A radiation-curable coating composition according to claim 25, which additionally contains (C) from 0.1% to 3.0% by weight of an organofunctional silane adhesion promoter and (D) optionally from 1.0% to 10.0% by weight of a photoinitiator wherein all of the stated percentages by weight are based on the total weight of (A), (B), (C) and (D).

5 27. A radiation-curable coating composition for an optical fiber comprising
 (A) from 10% to 90% by weight of an acrylated or methacrylated urethane oligomer which is the reaction product of (i) a polyether polyol; (ii) an aliphatic polyisocyanate; and (iii) an endcapping monomer selected from the group consisting of hydroxylalkylacrylate and hydroxylalkylmethacrylate;
 10 (B) from 5% to 80% by weight of one or more acrylate or methacrylate monomer diluents;
 (C) from 0.1% to 3.0% by weight of an organo-functional silane adhesion promoter; and
 (D) optionally, from 1.0% to 10% by weight of a photoinitiator,
 wherein all of the stated percentages are percentages by weight based on total weight of (A), (B), (C) and (D).

15 28. A radiation-curable coating for an optical fiber wherein said coating, after radiation cure, swells less than about 40% in length after soaking for four hours in gasoline at room temperature.

20 29. A process for preparing a coated optical fiber comprising
 (1) applying to an optical glass fiber a primary coating layer of a composition according to any one of claims 1 to 28; and
 (2) radiation-curing said coating in situ.

25 30. A process according to claim 29, additionally comprising applying atop said primary coating composition layer, before radiation curing, a secondary coating layer comprising
 (I) from 10% to 90% by weight of an aliphatic urethane oligomer based on a polyester and/or polyether and containing a reactive terminus;
 (II) from 20% to 60% by weight of a hydrocarbonaceous viscosity-adjusting component capable of reacting with the reactive terminus of (I);
 30 (III) optionally, from 0.05% to 10.0% by weight of a photoinitiator,
 wherein all of the stated percentages are percentages by weight based on total weight of (I), (II) and (III).

35 31. A coated optical fiber comprising
 (a) a glass optical fiber;
 (b) a radiation-cured primary coating layer comprising the cured reaction product of a composition according to any one of claims 1 to 28; and
 (c) a radiation-cured secondary coating layer comprising the cured reaction product of
 (I) from 10% to 90% by weight of an aliphatic urethane oligomer based on a polyester and/or polyether and containing a reactive terminus;
 40 (II) from 20% to 60% by weight of a hydrocarbonaceous viscosity-adjusting component capable of reacting with the reactive terminus of (I);
 (III) optionally, from 0.05% to 10.0% by weight of a photoinitiator,
 wherein all of the stated percentages are percentages by weight based on total weight of (I), (II) and (III).

45 32. A coated optical fiber according to claim 31, comprising
 (a) a glass optical fiber;
 (b) a radiation-cured primary coating layer comprising the cured reaction product of
 (A) from 10% to 90% by weight of an acrylated or methacrylated urethane oligomer which is the reaction product of (i) a polyether polyol; (ii) an aliphatic polyisocyanate; and (iii) an endcapping monomer selected from the group consisting of hydroxylalkylacrylate and hydroxylalkylmethacrylate;
 50 (B) from 5% to 80% by weight of one or more acrylate or methacrylate monomer diluents;
 (C) from 0.1% to 3.0% by weight of an organo-functional silane adhesion promoter; and
 (D) optionally, from 1.0% to 10% by weight of a photoinitiator,
 wherein all of the stated percentages are percentages by weight based on total weight of (A), (B), (C) and (D); and



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⑮ Organic solvent and water resistant, thermally, oxidatively and hydrolytically stable
radiation-curable coatings for optical fibers, optical fibers coated therewith and processes for
making same.

⑯ Ultraviolet radiation-curable primary coating
compositions for optical fibers are disclosed. The
primary coatings comprise a polyether polyol-based
reactively terminated aliphatic urethane oligomer;
one or more diluent monomers terminated with at
least one end group capable of reacting with the
reactive terminus of the oligomer; an organofunc-
tional silane adhesion promoter; and an optical
photoinitiator. Also disclosed are optical fibers coat-
ed with the coatings of the invention, and processes
for preparing same.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 92 31 0515

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)		
A	<p>DATABASE WPI Week 8525, Derwent Publications Ltd., London, GB; AN 85-150469 & JP-A-60 083 909 (NITTO ELECTRIC IND) 13 May 1985 * abstract *</p> <p>-----</p>	1,3,31			
<hr/>					
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<p>TECHNICAL FIELDS SEARCHED (Int.Cl.)</p>					
<hr/>					
<p>The present search report has been drawn up for all claims</p>					
Place of search	Date of compilation of the search	Examiner			
THE HAGUE	24 October 1994	Puettz, C			
<p>CATEGORY OF CITED DOCUMENTS</p>					
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p>					
<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>					

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